

Chemical Fingerprinting of Materials Developed Due to Environmental Issues

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Abstract

Instrumental chemical analysis methods are developed and used to chemically fingerprint new and modified External Tank materials made necessary by changing environmental requirements. Chemical fingerprinting can detect and diagnose variations in material composition. To chemically characterize each material, fingerprint methods are selected from an extensive toolbox based on the material's chemistry and the ability of the specific methods to detect the material's critical ingredients. Fingerprint methods have been developed for a variety of materials including Thermal Protection System foams, adhesives, primers, and composites.

Introduction

Some of the materials used in the Space Shuttle External Tank have been or will be replaced or modified due to environmental restrictions impacting the availability of raw materials. For example, External Tank Thermal Protection System (TPS) urethane foams originally containing CFC-11 blowing agent have been replaced with foams containing HCFC-141b blowing agent. Materials such as the TPS foams are critical to the performance of External Tank and, therefore, must be adequately tested to ensure that materials variations are detected before the material is used. Material variations can be due to a number of occurrences such as formulation changes, ingredient substitutions, material degradation, contamination, and mislabeling. A material can be simple such as a solvent, or complex such as a urethane foam that contains multiple ingredients (blowing agent, polyols, flame retardants, catalysts, surfactant) that in turn contain multiple ingredients.

Traditional tests used to characterize materials can be grouped into several categories. Traditional wet chemical tests are based on titrimetric or gravimetric procedures and include tests such as the hydroxyl number test for reactive polyol and the amine equivalent test for reactive isocyanate groups in urethane foam formulations. Physical property tests include viscosity, specific gravity, color, haze, and particle size measurements. Mechanical property tests include compressive strength, tensile strength, and hardness measurements. Although the traditional tests are extremely valuable and may indicate the presence of material variations, traditional tests alone cannot identify the exact nature and origin of the variation. Instrumental chemical analysis or chemical fingerprinting can both detect and diagnostically identify variations in chemical composition.

Chemical Fingerprinting Techniques

Chemical fingerprinting techniques most frequently used to characterize materials used on the External Tank program are identified in Table 1. These techniques are used to qualitatively (What's there?) or quantitatively (How much is there?) characterize materials.

Spectroscopic techniques are based on the interaction between light (electromagnetic radiation) and matter and are used to obtain information about elemental or molecular composition. Elements or compounds within a sample absorb or emit light of specific energy and intensity. The energy of the emitted or absorbed light (measured as a frequency or wavelength) is used to identify the elements or compounds present. The intensity of the emitted or absorbed light is related to the amount or concentration of the detected component. Spectroscopic techniques most commonly used are of two types: techniques that are used to identify elements present (examples: atomic emission, atomic absorption, and x-ray fluorescence spectroscopy) and techniques that are used to identify molecular compounds present (examples: infrared and Raman spectroscopy, mass spectrometry).

In a chromatographic procedure, the sample is dissolved or dispersed in a mobile phase, then passed through a column containing a stationary phase. Components within the sample are separated from one another based on the relative affinity of the components for the stationary phase. The mobile phase is either a gas (gas chromatography) or a liquid (high performance liquid chromatography, ion chromatography, gel permeation chromatography). In gas chromatography separated components are most often detected as changes in thermal conductivity or flame ionization current, whereas in liquid chromatography the separated components are usually detected as changes in ultraviolet absorption, refractive index, or conductivity.

Table 1. Fingerprint Techniques

Technique (Acronym)	Applications/Advantages	Limitations/Disadvantages
Atomic Absorption Spectroscopy (AA)	Elemental quantitative analysis Rapid analysis of single element High sensitivity for some elements Inexpensive	Not applicable to most nonmetal elements Small linear response range High matrix interference Solution usually required Sample preparation time consuming Special accessory required for solids
Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP/AES)	Simultaneous multi-element analysis Large linear response range Better than AA for refractory mat's	Limited sensitivity to non-metals Solution usually required Sample preparation time consuming Special accessory required for solids Expensive
X-ray Fluorescence Spectroscopy (XRF)	All elements of atomic number ≥ 11 Minimal sample preparation Applicable to solids and liquids Inexpensive	Not applicable to elements of atomic number < 11 without modifications
Infrared Spectroscopy (IR or FTIR)	Molecular identification Functional group identification Applicable to solids, liquids, gases Minimal sample preparation Extensive reference spectra libraries Inexpensive	Minor components masked by major Molecule must undergo dipole moment change during vibration
Raman Spectroscopy	Molecular identification Functional group identification Applicable to solids, liquids Applicable to aqueous solutions Minimal sample preparation	Not applicable to highly colored samples and samples that fluorescence Limited reference spectra libraries Molecule must undergo polarizability change during vibration Expensive
Mass Spectrometry (MS)	Identification of organic compounds Widely applicable to volatiles Extensive reference spectra libraries	Special sample introduction required for non-volatile samples Expensive
Gas Chromatography (GC)	Separation of multi-component mixtures of volatile compounds for quantitative analysis or for identification by tandem techniques Selectivity general or specific Inexpensive	Not applicable to non-volatile compounds without derivatization Not applicable to thermally unstable materials
High Performance Liquid Chromatography (HPLC)	Separation of multi-component mixtures of soluble compounds for quantitative analysis or for identification by tandem techniques	Method development time-consuming Sample must be soluble in suitable solvent Large volume of waste solvent Moderately expensive
Ion Chromatography (IC)	Separation of complex mixtures of ionic species for quantitative analysis Applicable to organic and inorganic More sensitive than wet methods	Method development time-consuming Moderately expensive
Gel Permeation Chromatography (GPC)	Separation of complex mixtures based on molecular size Determination of molecular weight	Sample must be soluble in suitable solvent Large volume of waste solvent GPC columns expensive

Applications of Chemical Fingerprinting to Simple and Complex Materials

The chemical fingerprint techniques listed in Table 1 are not all used for each material. Instead, a combination of techniques is selected based on the material's chemical composition and its physical properties. One or two techniques may be sufficient to adequately identify and monitor the composition of a relatively simple material, while a combination of several techniques may be required for more complex materials.

An example of a simple material is the solvent HCFC-225, which is a mixture of two isomers, HCFC-225ca and HCFC-225cb. Gas chromatography readily separates the two isomers from one another and from low concentration impurities. This technique is used to measure the percent purity of the HCFC-225 and to measure the ratio of the two isomers. Gas chromatography is also used to measure the percent purity of HCFC-225G, which is composed predominantly of the HCFC-225cb isomer.

Urethane foams comprising the External Tank Thermal Protection System (TPS) are examples of complex materials that cannot be totally characterized by a single fingerprint technique. Several TPS foam materials containing CFC-11 as blowing agent were modified or replaced by materials containing HCFC-141b. These materials are received as two liquid components. One of the components contains methylene diphenylene diisocyanate (MDI) and its oligomers and is frequently referred to as Component A. The other component, frequently called Component B, may be a complex mixture of polymeric alcohol (polyols), flame retarding ingredients, blowing agents, catalysts, and surfactants. Ingredients may be in the formulation at widely different concentrations ranging from less than one percent to up to nearly seventy percent by weight. More than one of each type of ingredient may be present, and ingredients themselves may be multi-component. In addition, the ingredients are very different from one another chemically and therefore require the use of different fingerprinting techniques. To completely characterize the material, a combination of techniques capable of detecting each key ingredient in the formulated material must be identified.

The combination of fingerprinting techniques that may be required to characterize a complex urethane formulation is presented in Table 2. The goal of the fingerprinting program is to identify and develop a group of techniques that adequately and efficiently characterizes the material. Often, a single procedure can target several ingredients. For example, an inductively coupled plasma atomic emission spectroscopic (ICP/AES) procedure can be used to measure concentrations of elements such as phosphorus present in flame retardants, silicon present in silicone surfactants, and metals such as tin, lead, or potassium present in catalysts. On the other hand, an ingredient that is both present at a low concentration and inherently difficult to detect due to its chemistry may necessitate the development of a procedure that targets that ingredient alone. Examples include a low concentration amine catalyst that requires a gas chromatographic procedure with a specialized nitrogen-phosphorus detector (NPD) or low concentration bromine-containing flame retarding compound that requires a special high performance liquid chromatographic (HPLC) procedure.

Table 2. Fingerprinting Techniques to Characterize Generic Foam Formulation, Component B

Generic Ingredient	Typical Concentration	Fingerprint Techniques	Chemistry Measured
Polyols	5 - 70%	FTIR GPC HPLC GC	Functional Groups (Polyol Identification) Polymer Molecular Weight, Concentration Concentration Based on Detected Components Concentration Based on Volatile Components
HCFC Blowing Agent	15 - 35	GC FTIR	Concentration of Volatile HCFC Functional Groups (Blowing Agent Identification)
Amine Catalysts	0.2 - 3.0	GC	Concentration of Volatile Amines
Organo-metallic Catalysts	0.2 - 0.6	ICP/AES	Elemental Concentration Related to Catalyst Conc.
Silicone Surfactant	1 - 2	ICP/AES	Silicon Concentration Related to Surfactant Conc.
Phosphorus-Containing Flame Retardants	2 - 20	GC ICP/AES	Concentration of Volatile Flame Retardant Phosphorus Concentration Related to Fl. Ret. Conc.
Halogen-Containing Flame Retardants	1 - 10	GC HPLC	Concentration Based on Volatile Components Concentration of Halogen Compound

Supplier Partnership

Partnership with our suppliers is a key component in our fingerprinting program. Important steps in developing fingerprint methods for a given material are identifying the formulation ingredients and understanding each ingredient's role in the formulation. In some cases, ingredients are identified in the Material Safety Data Sheet or in other easily obtained documents. When the material is a simple mixture of relatively simple ingredients, fingerprint analysis may readily identify ingredients. However, in most cases, especially when materials are composed of complex mixtures of complex ingredients, the supplier's cooperation is needed. For the most part, our suppliers have been willing to identify the ingredients in their materials, to disclose ingredient concentrations, and to provide samples of ingredients. This cooperation has greatly expedited fingerprint method development. By fingerprinting a material's ingredients, the peaks in the material's chromatograms and spectra can be assigned to individual ingredients, and changes in the material's fingerprint can be readily attributed to specific ingredients. When material problems arise, fingerprinting data can be relayed back to the supplier in order to expedite resolution of the problem. Supplier partnership is based on the understanding that formulation information will be used only to better understand the material's chemistry and to develop methods to ensure material consistency, and that proprietary information will not be disclosed without the supplier's agreement.

Fingerprint Databases

Fingerprinting of a material yields data that is compiled into a quantitative database for that material. Fingerprint databases provide a baseline reference that are used to detect and identify lot-to-lot variations in composition that may be due to formulation changes, material degradation, or contamination. When a sufficient number of lots have been fingerprinted, the database is used to select fingerprint methods for implementation as receiving/acceptance tests and to establish receiving/acceptance ranges. Fingerprint methods and databases are also used to support material failure investigations, new material development, alternate material qualification, new supplier qualification, new manufacturing location qualification, and material shelf-life investigations.

Fingerprint databases provide a reservoir of data that can be used to generate control charts. Through the use of control charts, shifts or trends in material parameters can be detected early, before the material fails to meet specification.

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